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## **FINAL REPORT**

Department of Defense EPSCoR Award, administered through AFOSR/NL

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Start Date: 1-June-1996

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### **Interactions of Hyperthermal Oxygen Atoms with Polymer Surfaces**

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## Objectives

**Source characterization.** The presence of metastable atomic and molecular oxygen species and their fractions in the hyperthermal oxygen beam source will be determined.

**Interaction dynamics of atomic oxygen with model surfaces.** A series of molecular beam-surface scattering experiments, with mass spectrometric detection of volatile reaction products, will be conducted with atomic oxygen beams impinging on polypropylene and liquid squalane surfaces. Fundamental questions about the reactions of energetic oxygen atoms with hydrocarbon surfaces will be answered, and the experimental results will be compared with theoretical calculations.

**Polymer etching for optoelectronic devices.** The hyperthermal oxygen beam will be used to etch ridge waveguides into polymer films. Scanning electron microscopy will be used as a probe in order to optimize the process of producing structures with straight and smooth sidewalls. Etched waveguides will be sent to JPL for optical loss measurements. An assessment of the efficacy of directed neutral beams to produce superior waveguides will be made.

**Surface chemistry modification.** The possibilities of the hyperthermal atomic oxygen beam to create specific and/or novel oxide functionalities on polymer surfaces will be explored by exposing polymer surfaces to the O-atom beam and identifying the resulting surface chemical modifications with various surface analytical techniques. The beam-induced modifications will be compared with modifications produced in a more conventional plasma environment.

**Space environmental effects: atomic oxygen testing.** The PI will convey information gained from various studies on hyperthermal atom-surface interactions to the space environmental effects community in order to improve the general understanding of atomic oxygen reactions with spacecraft materials in low Earth orbit and to define better test standards for ground-based assessment of candidate spacecraft materials.

## Summary of Efforts

All objectives of the project were met or exceeded, with the exception of the source characterization. This project directly contributed to many publications and presentations. In addition, several students have been supported, and a number of collaborations have been advanced. We have answered many fundamental questions about the initial reactions with a hydrocarbon surface; related theoretical calculations have been completed and published by another group; waveguide-like structures have been etched; modification of polystyrene surfaces has been performed in plasma and hyperthermal beam environments and the resultant chemistries compared; yeast-cell adhesion studies have been conducted on beam- and plasma-modified surfaces; a detailed study on the effect of ion-implantation on the reactivity of polymer surfaces with atomic oxygen has been completed; activity in the space environmental effects community has remained high; and related studies of the interaction of fast fluorine and oxygen atoms with a silicon surface have been completed.

## Accomplishments/New Findings

### *Research highlights*

**Source characterization.** Nothing substantial and new has been added to our understanding of the hyperthermal atomic oxygen source. However, the tools available for characterizing the electronic states of the species in the source were augmented considerably by the donation of a Nd:YAG-pumped dye laser and harmonic generation system from the University of Zürich in Switzerland. This laser provides the PI with the capability to conduct multiphoton ionization studies on the atomic or molecular oxygen in the beam in order to determine the fraction of ground-state triplet versus electronically-excited singlet species.

**Interaction dynamics of atomic oxygen with model surfaces.** A very successful experiment was conducted in Prof. Piergiorgio Casavecchia's lab in Perugia, Italy, where supersonic beams of relatively low translational energy atoms ( $<1$  eV) were directed at target surfaces. The initial reactive events of an O atom incident on a hydrocarbon surface were studied with the use of a continuously refreshed liquid hydrocarbon (squalane) surface. Effects of continuous atomic oxygen bombardment were also studied by directing an atomic oxygen beam at a static polypropylene surface. Products that scattered from each surface were detected with a rotatable quadrupole mass spectrometer detector, and time-of-flight distributions at various incident and exit angles were collected. Reactive product signals were observed at mass-to-charge ratios ( $m/z$ ) of 17 ( $\text{OH}^+$ ), 18 ( $\text{H}_2\text{O}^+$ ), 28 ( $\text{CO}^+$ ), and 44 ( $\text{CO}_2^+$ ). The only significant products from the reaction of O atoms with the continuously refreshed liquid surface were detected at  $m/z = 17$  and 18. The dynamics of the interactions of atomic chlorine with the squalane surface were investigated and compared to the results of the analogous study of O-atom interactions. Further experiments on the interaction of hyperthermal O atoms (translational energies  $\sim 5$  eV) with liquid and solid polymer surfaces were subsequently conducted in the PI's lab. Reactions of hyperthermal O atoms with hydrocarbon surfaces were qualitatively similar to those employing lower energy O atoms, although the quantitative dynamics differed significantly.

Time-of-flight distributions of the initial reaction products revealed that all products were formed in two populations, those leaving the surface hyperthermally and those exiting the surface after achieving thermal equilibrium. The dynamical properties of the hyperthermal OH product indicate that it is formed through a direct abstraction (Eley-Rideal) mechanism. The hyperthermal  $\text{H}_2\text{O}$  signal could not correspond to a single collision mechanism. The sum of two direct reactions: the initial formation of OH, with subsequent abstraction of another H atom, is the likely explanation for the production of hyperthermal  $\text{H}_2\text{O}$ . The most probable explanation for the thermal OH is that direct abstraction is followed by thermal accommodation of the OH product on the surface. Once the OH becomes accommodated on the surface, it may desorb thermally or abstract another hydrogen atom to form  $\text{H}_2\text{O}$ , which would then also desorb thermally. With these data, we can conclude that the first step toward volatile reaction products, whether thermal or hyperthermal, is a direct reaction to form OH. In the reaction of Cl with a squalane surface, the HCl time-of-flight distributions also revealed thermal and hyperthermal interaction channels, in analogy to the dynamical behavior of the

OH signals observed in the reaction of atomic oxygen with squalane. The thermal product may arise from two mechanisms: 1) desorption of trapped HCl product and 2) reaction of trapped Cl atoms to form thermal HCl, which subsequently desorbs. The hyperthermal signal is again the result of an Eley-Rideal direct-abstraction mechanism. The HCl and OH hyperthermal products were scattered preferentially in the specular direction in the laboratory frame. However, a kinematic analysis showed a propensity for scattering sideways or even backwards (with respect to the direction of the incident atomic beam) in the center-of-mass (c.m.) frame. The kinematic analysis also allowed the determination of the effective mass of the surface collision partner, the c.m. collision energy, and the final c.m. translational energy. Similar c.m. scattering dynamics have been observed in gas-phase reactions of O and Cl atoms with saturated hydrocarbons. Theoretical modeling on the interaction of oxygen atoms with a saturated hydrocarbon surface was inspired by this experimental work and was taken up by Prof. William Hase of Wayne State University. The theoretical work substantially confirms the conclusions reached from the experiments. It has recently been published in the *Journal of Molecular Structure*.

The sequence of reactions that leads to material removal is considerably more complex than the initial interactions. We have seen that these reactions ultimately lead to formation of volatile CO and CO<sub>2</sub> products. A new phenomenon that was discovered as part of the DEPSCoR project is that the rate of CO and CO<sub>2</sub> production is significantly enhanced when high-energy ( $\geq 8$  eV) Ar atoms or N<sub>2</sub> molecules collide with a surface that is undergoing continuous oxidation. The detailed nature of this collisional process is currently under investigation as part of a follow-on effort. Nevertheless, such a collisional process is expected to be very important in some exposure environments, (e.g., in space, where N<sub>2</sub> strikes oxidized surfaces with collision energies greater than 10 eV, or in etching apparatuses, where relatively low energy ions may bombard an oxidized surface).

**Polymer etching for optoelectronic devices.** Masked polymer samples, supplied by Dr. Joe Perry of JPL (now at the University of Arizona), were etched in the hyperthermal atomic oxygen beam. Various exposure conditions were used to find optimum processing conditions. We identified problems with neutral beam etching of polymers that are related to secondary reactions of inelastically scattered oxygen atoms. The etched sidewalls were rougher than expected, and the mask was undercut. Therefore, no studies of optical loss of etched waveguides were pursued.

The newly discovered collisional effect, mentioned above, may point the way to a new process that would etch features in polymers with straight sidewalls. There is a potentially major advantage to using Ar to remove material collisionally from a surface undergoing reaction because etch products will be removed efficiently, leaving more reactive sites, and because inelastic scattering of fast Ar will not lead to sidewall undercutting as would inelastic scattering of energetic etchant atoms.

**Surface chemistry modification.** Parallel studies of the surface chemical modification of polystyrene surfaces and of yeast cell adhesion to these surfaces have been completed. We observed that oxidation of polystyrene surfaces in an oxygen plasma and in the hyperthermal oxygen beam led to similar amounts of surface oxidation that reached a steady state in a short time. However, the distribution of carbon-oxygen bonding environments differed markedly between plasma and beam

exposures. The molecular beam exposure produced unique metastable species that persisted up to two weeks. After aging, the key effect of exposure duration on the sample surfaces was on surface roughness, with roughness proportional to exposure fluence. Cell adhesion experiments showed that the rate of cell accumulation on the plasma- and beam-exposed samples differed significantly even when the surface chemistry appeared to be very similar. Apparently, the cells detected a difference that was not obvious from X-ray photoelectron spectroscopy. In addition, for the same surface chemistry, increased surface roughness led to an increase in cell accumulation rate even though the rough features on the surface were more than an order of magnitude smaller than the size of the cell. A subsequent experiment showed that the chemical modification of polystyrene can be patterned and that yeast cells will adhere to the surface according to this pattern.

**Space environmental effects.** The PI has become a world-recognized leader in the area of atomic oxygen interactions with materials in the low-Earth-orbital space environment. He has been a speaker at numerous meetings on space environmental effects and has served on a panel that developed an ASTM Recommended Practice for atomic oxygen testing of candidate spacecraft materials. The knowledge generated by this DEPSCoR Grant was vitally important to a recent book chapter authored by the PI on polymer degradation in low Earth orbit. This book chapter has been distributed widely throughout the space environmental effects community and provides the most up-to-date review of the mechanisms of polymer erosion in low Earth orbit.

A collaboration with Dr. Masahito Tagawa of Osaka University (now at Kobe University) proved to be quite fruitful. Talks were presented and papers were written on two topics of importance to the space environmental effects community: 1) reduction in atomic oxygen reactivity at a surface through ion implantation and 2) the nature of the  $\text{SiO}_x$  film that forms on a silicon surface that is exposed to impingement by hyperthermal oxygen atoms. This latter topic is important because the majority of protection schemes for polymers in low Earth orbit use  $\text{SiO}_x$  coatings that are either applied before launch or are formed by reaction of a silicon-containing surface with O atoms on orbit.

**Related accomplishments.** Analysis was completed on data from an experiment on the inelastic scattering of hyperthermal fluorine atoms from a silicon surface. The findings from this research allowed us to draw some general conclusions about the important role of multiple-bounce scattering when etchant species strike a surface. It appears that analogous processes are occurring when fast oxygen atoms interact with a polymer surface. A paper was written and several talks were given on this work.

Some applied experiments were conducted in collaboration with Dr. J. Albert Schultz of Ionwerks, a small company in Houston, TX. These experiments dealt with the use of concentrators for accelerated testing and revealed that our intuition was wrong. Scattering processes in the conical concentrators inhibited O atoms from degrading a polymer on the other side rather than making them more potent at the output. It thus appears from this work that concentrating O atoms through gas-surface scattering processes in a cone-like structure is not a viable route to accelerated testing.



## ***Relevance and potential applications***

All the research discussed above directly supports the original goals, which are 1) to develop a microscopic understanding of the interactions of hyperthermal oxygen atoms with a hydrocarbon polymer surface and 2) to apply hyperthermal beam-surface studies to DoD and commercial goals, such as *a)* improved predictions of materials durability in Earth's upper atmosphere, *b)* tailored modifications of polymer surface chemistries, and *c)* new etch processes for fabrication of polymer waveguide optoelectronic devices.

The key relevance of the work to the Air Force is in the effect of chemical processes on operations in space. Atomic oxygen is one of the most important natural hazards of the low Earth orbital space environment, and though much phenomenological have been generated, little was known about how atomic oxygen attacks and degrades materials. Not until this research did anyone know what the initial reactions are when an energetic oxygen atom encounters a hydrocarbon surface. Our data have allowed us to infer these reactions, and our conclusions have been supported by theoretical work in another research group. In general, the knowledge generated by this work is at the forefront of our knowledge of how polymers degrade in low Earth orbit. Further work is ongoing in the PI's lab and this work coupled with complementary work on space environmental effects on materials in other groups (likely to be spurred on by the recent MURI call for proposals) should ultimately reveal the details of materials degradation from the initial events to macroscopic etching/degradation. This detailed knowledge will allow us to refine test parameters for ground-based testing of candidate materials. For example, testers still argue about the influence of incident O-atom energy and flux on a test or whether ions or VUV light play a significant synergistic role in assisting O atoms in the degradation of materials. An accurate picture of the reaction mechanisms will put this discussion to rest. Even test methods may be revised with increased understanding. One can imagine that a quantitative relationship could possibly be made between in situ analysis of reaction products, be they volatile or nonvolatile, and material durability if we only knew enough about the interaction. With such a relationship in hand, we could perform tests in a fraction of the time it takes to expose a sample and measure weight loss or recession or conduct some other post-exposure analysis. This instant analysis would provide the ultimate in accelerated and accurate testing that has been long sought after. The knowledge of how atomic oxygen attacks and degrades polymeric materials will undoubtedly aid in the development of new materials and/or protective coatings for current materials. In summary, increased understanding is vitally important for faster, more reliable testing and lower risk missions in space.

## **Personnel supported and associated with research effort**

### ***Montana State University***

**Terry Thompson** (surface modification), graduate student, salary support through NSF Center for Biofilm Engineering, resources provided by DEPSCoR grant. M.S. Degree in Chemistry awarded December 1997.

**Donna Garton** (fundamental studies), graduate student, supported full time for one year by DEPSCoR Grant (8/96 - 8/97), then supported by NASA fellowship. M.S. Degree in Chemistry awarded August 1998.

**James Seale** (polymer etching and fundamental studies), graduate student, supported approximately 2/3 time by DEPSCoR grant. M.S. Degree in Chemical Engineering awarded August 1998.

**Angela Frandsen** (cell adhesion, general lab assistance), performed cell adhesion studies as an undergraduate student, worked part-time as technician in PI's lab during the course of one year after earning a B.S. in Chemical Engineering in May 1997.

**Jianming Zhang** (fundamental studies), graduate student, supported full time for one year by DEPSCoR Grant (5/97 to 5/99), still pursuing degree of Ph.D. in Chemistry.

**Prof. Bonnie Tyler** (surface chemistry modification), collaborator at Montana State University on the surface chemical modification of polystyrene surfaces and yeast cell adhesion to the modified surfaces.

**Karen Wesenberg** (surface modification, cell adhesion), Prof. Tyler's graduate student who was involved in collaborative effort with PI's group.

### ***University of Perugia, Italy***

**Prof. Piergiorgio Casavecchia** (fundamental studies), collaborator on interactions of a supersonic atomic oxygen beam with a liquid hydrocarbon surface.

**Prof. Gian Gualberto Volpi**, director of entire research group of which Prof. Casavecchia is a member.

**Dr. Nadia Balucani**, staff scientist in Prof. Casavecchia's lab who was involved in collaboration with PI.

**Dr. Michele Alagia**, post-doc in Prof. Casavecchia's lab who was involved in collaboration with PI.

### ***Osaka University, Japan***

**Dr. Masahito Tagawa** (space environmental effects), collaborator on the effects of hyperthermal atomic oxygen on various surfaces.

### ***Caltech***

**Prof. Konstantinos Giapis** (related work), collaborator at Caltech on inelastic scattering of hyperthermal fluorine atoms on a silicon surface.



Teresa Moore, graduate student for Prof. Mitchio Okumura who participated in collaborative experiments with Prof. Giapis.

### ***Jet Propulsion Laboratory, Pasadena, CA***

Dr. Joseph W. Perry (polymer etching), collaborator who provided masked polymer samples that were etched in PI's lab.

### ***Boeing, Seattle, WA***

Dr. Harold G. Pippin (space environmental effects), Boeing scientist who funded atomic oxygen testing of Boeing-designed concentrators in PI's lab.

### ***Ionwerks, Houston, TX***

Dr. J. Albert Schultz (space environmental effects), president of a small company who has augmented PI's funding for testing the ability of a conical structure to concentrate atomic oxygen for accelerated testing and for growing novel oxide films.

## **Publications** (copies included at end of report)

### ***Peer-Reviewed***

- 1) "Inelastic Scattering Dynamics of Hyperthermal Fluorine Atoms on a Fluorinated Silicon Surface," T. K. Minton, K. P. Giapis, and T. A. Moore, *J. Phys. Chem. A* **101**, 6549-55 (1997).
- 2) "Reactive Scattering of Ground-State and Electronically-Excited Oxygen Atoms on a Liquid Hydrocarbon Surface," D. J. Garton, T. K. Minton, M. Alagia, N. Balucani, P. Casavecchia, and G. G. Volpi, *Discuss. Faraday Soc.* **108**, 387-99 (1997).
- 3) "Formation of Thin Oxide Films on Room-Temperature Silicon (100) by Exposure to a Neutral Beam of Hyperthermal Atomic and Molecular Oxygen," M. Tagawa, T. Ema, H. Kinoshita, M. Umeno, N. Omae, and T. K. Minton, *Jpn. J. Appl. Phys.* **37**, L1455-57 (1998).
- 4) "Comparative Dynamics of  $\text{Cl}(^2P)$  and  $\text{O}(^3P)$  Interactions with a Liquid Hydrocarbon Surface," D. J. Garton, T. K. Minton, M. Alagia, N. Balucani, P. Casavecchia, and G. G. Volpi, *J. Chem. Phys.* **112**, 5975-84 (2000).
- 5) "Collision-Assisted Erosion of Hydrocarbon Polymers in Atomic Oxygen Environments," T. K. Minton, J. Zhang, D. J. Garton, and J. W. Seale, *High Performance Polymers* **12**, 27-42 (2000).

- 6) "Dynamics of Atomic-Oxygen-Induced Polymer Degradation in Low Earth Orbit," T. K. Minton and D. J. Garton, in *Chemical Dynamics in Extreme Environments: Advanced Series in Physical Chemistry*, R. A. Dressler, ed. (World Scientific, Singapore, 2000).

### ***Theses, Technical Reports, and Conference Proceedings***

- 1) "Reactive Atom Etching of Polymers," J. W. Seale, T. K. Minton, and J. W. Perry, *Polymer Preprints* **38**, 1089 (1997).
- 2) "A Comparison of Oxidized Polystyrene Surfaces Produced by Plasma and Neutral Beam Methods," T. L. Thompson, B. J. Tyler, and T. K. Minton, *Polymer Preprints* **38**, 1063 (1997).
- 3) "Oxidation of Room Temperature Silicon (001) Surfaces in a Hyperthermal Atomic Oxygen Beam," M. Tagawa, T. Ema, H. Kinoshita, M. Umeno, N. Omae, and T. K. Minton, in *Proceedings of the Seventh International Symposium on Materials in the Space Environment*, Toulouse, France, June 16-20, 1997.
- 4) "Atomic Oxygen Interactions with Saturated Hydrocarbon Surfaces," D. J. Garton, T. K. Minton, M. Alagia, P. Casavecchia, and G. G. Volpi, in *Proceedings of the 1997 American Institute for Aeronautics and Astronautics Conference & Exhibit*, Huntsville, AL, September 23-25, 1997; paper 97-3947.
- 5) "Oxidized Polystyrene Surfaces Produced by Plasma and Neutral Beam Methods: an X-Ray Photoelectron and Surface Derivatization Study," Terry L. Thompson, M.S. Thesis, December 1997.
- 6) "Dynamics of Atomic-Oxygen-Induced Degradation of Materials," T. K. Minton, J. W. Seale, D. J. Garton, and A. K. Frandsen, in *Proceedings of the 4<sup>th</sup> International Conference on the Protection of Materials and Structures from the Low Earth Orbital Space Environment*, Toronto, Canada, April 23-24, 1998.
- 7) "Reactive Scattering of Oxygen and Chlorine Atoms on Hydrocarbon Surfaces," Donna J. Garton, M.S. Thesis, August 1998.
- 8) "Etching of Hydrocarbon Polymers with Hyperthermal Neutral Beams," James W. Seale, M.S. Thesis, August 1998.
- 9) "Mechanisms of Polymer Erosion in Low Earth Orbit: Implications for Ground-Based Testing," T. K. Minton, J. W. Seale, D. J. Garton, and J. Zhang, in *Proceedings of the 44<sup>th</sup> International SAMPE Symposium & Exhibition*, Long Beach, CA, May 23-27, 1999.

- 10) "Materials Degradation in Low Earth Orbit: An Oxygen Atom's Accomplice," T. K. Minton, D. J. Garton, J. Zhang, and J. W. Seale, in *Proceedings of the 6<sup>th</sup> Japan International SAMPE Symposium & Exhibition (JISSE-6)*, Tokyo Big Sight, Tokyo, Japan, October 26-29, 1999.
- 11) "Atomic-Oxygen Interactions with Saturated Hydrocarbon Surfaces: Probing Polymer Degradation Mechanisms," D. J. Garton, J. Zhang, and T. K. Minton, in *Proceedings of the 8<sup>th</sup> International Symposium on Materials in a Space Environment and 5<sup>th</sup> International Conference on Protection of Materials and Structures from the LEO Space Environment*, Arcachon, France, June 5-9, 2000.

### ***Reports published on web***

- 1) "Surface degradation of Ion-Implanted Films by a Hyperthermal Oxygen Atom Beam," M. Tagawa and T. K. Minton (1997).
- 2) "Adhesion of *Candida albicans* to Oxidized Polystyrene," A. K. Frandsen, T. K. Minton, and B. J. Tyler (1997).

## **Interactions/Transitions**

### ***Participation/presentations at meetings, conferences, seminars, etc.***

(PI and PI's group members only)

- 1) "The Laser Detonation Neutral Beam Source: Assessment of Performance via Mass Spectrometry," *Methodologies for Ground Simulation of the Space Environment*, Southampton, UK, July 17-19, 1996. (contributed talk)
- 2) "Protocol for Atomic Oxygen Testing of Materials in Ground-Based Facilities," *Methodologies for Ground Simulation of the Space Environment*, Southampton, UK, July 17-19, 1996. (contributed talk)
- 3) "Inelastic Scattering During Etching of Silicon with Hyperthermal Fluorine Atoms," *212<sup>th</sup> American Chemical Society National Meeting*, Orlando, FL, August 25-29, 1996. (contributed talk)
- 4) "Inelastic Scattering During Etching of Silicon with Hyperthermal Fluorine Atoms," Dipartimento di Chimica, Università di Perugia, Perugia, Italy, November 14, 1996. (invited seminar)
- 5) "Inelastic Scattering During Etching of Silicon with Hyperthermal Fluorine Atoms," Physikalische-Chemisches Institut der Universität Zürich, Switzerland, November 22, 1996. (invited seminar)

- 6) "Inelastic Scattering Dynamics of Hyperthermal Fluorine Atoms on a Fluorinated Silicon Surface," *International Symposium on Modern Trends in Chemical Dynamics*, Academia Sinica, Taipei, Taiwan ROC, December 8-12, 1996. (poster)
- 7) "Reactive Atom Etching of Polymers," *213<sup>th</sup> American Chemical Society National Meeting*, San Francisco, CA, April 13-17, 1997. (contributed talk presented by student, PI attended)
- 8) "A Comparison of Oxidized Polystyrene Surfaces Produced by Plasma and Neutral Beam Methods," *213<sup>th</sup> American Chemical Society National Meeting*, San Francisco, CA, April 13-17, 1997. (contributed talk presented by student, PI attended)
- 9) "Adhesion of *Candida albicans* to Modified Polystyrene," *213<sup>th</sup> American Chemical Society National Meeting*, San Francisco, CA, April 13-17, 1997. (contributed talk presented by student, PI attended)
- 10) "Inelastic Scattering During Etching of Silicon with Hyperthermal Fluorine Atoms," Department of Chemistry, University of Montana, Missoula, MT, May 5, 1997. (invited seminar)
- 11) "Reactive Scattering of Oxygen Atoms on Saturated Hydrocarbon Surfaces," *1997 Conference on the Dynamics of Molecular Collisions*, Brainerd, MN, July 21-25, 1997. (poster presented by student, PI attended)
- 12) "Reactive Scattering of Oxygen and Chlorine Atoms on Hydrocarbon Surfaces," *Gordon Research Conference on Dynamics at Surfaces*, Andover, NH, August 10-14, 1997. (poster presented by student, PI attended)
- 13) "Reactive Scattering of Oxygen Atoms on a Liquid Hydrocarbon Surface," *214<sup>th</sup> American Chemical Society National Meeting*, Las Vegas, NV, September 7-11, 1997. (contributed talk)
- 14) "Atomic Oxygen Interactions with Saturated Hydrocarbon Surfaces," *1997 American Institute of Aeronautics and Astronautics Conference and Exhibit*, Huntsville, AL, September 23-25, 1997. (invited talk)
- 15) "Reactive Scattering of Atomic Oxygen and Chlorine from Saturated Hydrocarbon Surfaces," D. J. Garton, T. K. Minton, M. Alagia, N. Balucani, P. Casavecchia, and G. G. Volpi, *Analytical/Physical/Inorganic Seminar*, Department of Chemistry and Biochemistry, Montana State University, Bozeman, MT, October 24, 1997. (seminar presented by student)
- 16) "Reactive Scattering of Ground-State and Electronically-Excited Oxygen Atoms on a Liquid Hydrocarbon Surface," *Faraday Discussion 108*, University of Sussex, Brighton, UK, December 15-17, 1997. (presenter)

- 17) "Reactive Scattering of Atomic Oxygen and Chlorine from Hydrocarbon Surfaces," Dipartimento di Chimica, Università di Perugia, Perugia, Italy, December 19, 1997. (invited seminar)
- 18) "Reactive Scattering of Oxygen Atoms from Saturated Hydrocarbon Surfaces," *Montana Section of the American Chemical Society Annual Meeting*, Bozeman, MT, April 12, 1998. (contributed talk presented by student)
- 19) "Dynamics of Atomic-Oxygen-Induced Degradation of Materials," *4<sup>th</sup> International Conference on the Protection of Materials and Structures from the Low Earth Orbital Environment*, Toronto, Canada, April 23-24, 1998. (invited talk)
- 20) "Reactive Scattering of Atomic Oxygen on Hydrocarbon Surfaces," AFOSR Molecular Dynamics Contractor's Review, Monterey, CA, May 17-20, 1998. (invited talk)
- 21) "Reactive Scattering Dynamics of Fast Atoms with Hydrocarbon Surfaces: Initial and Steady-State Reactions," Department of Chemistry, Northwestern University, Evanston, IL, October 23, 1998. (invited seminar)
- 22) "Reactive Scattering Dynamics of Fast Atoms with Hydrocarbon Surfaces: Initial and Steady-State Reactions," Department of Chemistry University of Wisconsin, Madison, WI, October 27, 1998. (invited seminar)
- 23) "Reactive Scattering Dynamics of Fast Atoms with Hydrocarbon Surfaces: Initial and Steady-State Reactions," Department of Chemistry, Ohio State University, Columbus, OH, October 30, 1998. (invited seminar)
- 24) "Inelastic and Reactive Scattering Dynamics of Hyperthermal Oxygen Atoms on a Liquid Hydrocarbon Surface," *Montana Section of the American Chemical Society Annual Meeting*, Bozeman, MT, April 24, 1999. (contributed talk presented by student)
- 25) "Mechanisms of Polymer Erosion in Low Earth Orbit: Implications for Ground-Based Testing," *44<sup>th</sup> International SAMPE Symposium and Exhibition*, Long Beach, CA, May 25, 1999. (contributed talk)
- 26) "Reactive Scattering Dynamics of Fast Atoms with Hydrocarbon Surfaces: Initial and Steady-State Reactions," Department of Chemistry and Biochemistry, University of California at San Diego, La Jolla, CA, May 28, 1999. (invited seminar)

### ***Consultative and advisory functions***

During 1997, the PI was a consultant to the Jet Propulsion Laboratory and assisted in writing a report on the atomic oxygen component of the JPL Space Environments and Effects program to the Ballistic Missile Defense Organization/Innovative Science and Technology Office. The contact person at JPL was Dr. Joseph W. Perry.

The PI served on a panel that was organized by Cliff Cerbus of Air Force Wright Laboratories to develop an ASTM Recommended Practice for atomic oxygen testing of materials. This new standard was published in 2000.

### ***Transitions***

**Ionwerks**. Ionwerks is a small company in Houston, Texas that is involved in time-of-flight mass spectrometry, surface characterization by ion scattering, and film growth on surfaces. Because of the experience and capabilities of the PI in scattering of hyperthermal atomic oxygen from surfaces, the president of Ionwerks, Dr. J. Albert Schultz, enlisted the help of the PI for the evaluation of conical atomic oxygen concentrators that were proposed to be used in space or in conventional processing facilities for concentrating oxygen atoms and growing novel oxide films. Ionwerks was also interested in having the PI characterize a source of fast neutrals that is based on the neutralization and slowing of fast ions as the ions scatter from a metal surface. The work began as a low-level collaboration with them on their Phase I NASA SBIR, and it continued with funding from them for a collaboration on their Phase II proposal.

As an initial test of an atomic oxygen concentrator developed by Ionwerks, five identical cone-like concentrators with a concentration factor of 256 were flown in low Earth orbit on the Wake Shield Facility in 1996. Samples of Kapton (a polyimide polymer) were placed in an open area and at the output of the concentrators. By measuring the post-exposure erosion depth of the Kapton samples, an assessment of the effectiveness of the concentrator was made. Performing an analogous experiment at Montana State University allowed for a comparison of the extent of erosion on the lab- and space-exposed samples.

The etch depths of the space-exposed samples were measured at the Space Vacuum Epitaxy Center (SVEC) in Houston. The control sample (no O-atom concentration) had an etch depth of 0.6  $\mu\text{m}$ , while the samples placed at the output of the concentrators were significantly less etched, 0.2 - 0.4  $\mu\text{m}$ . It should be noted, however, that the retrieved cones showed evidence of contamination from venting of GaAs and other materials. The ground-based experiment was performed on one of the concentrators flown on the Wake Shield Facility. The average O-atom flux was similar to the space flux, approximately  $0.5 \text{ monolayers s}^{-1}$ . Kapton samples were placed at the output of the cone and in an open area, as was done in the space experiment. Again, etch depths were somewhat greater for the control than for the sample under the concentrator.



Another concentrator with a lower concentration factor of about 12 was flown in conjunction with a pressure gauge on the Wake Shield Facility. The pressure at the output of the cone was about a factor of 10 higher than the ambient pressure, indicating O-atom concentration almost as much as the concentration factor, which is the ratio of areas between the input and output ends of the cone. Kapton etching through a concentrator with a factor of 11 concentration was also performed in the lab, and again the control had a greater etch depth than the sample at the output of the concentrator: 1.8  $\mu\text{m}$  for the control versus 1.5  $\mu\text{m}$  under the concentrator.

These preliminary results indicate that the concentrators may be slowing down the O atoms so much that they no longer have enough energy to react. Studies of O-atom inelastic scattering from metal surfaces indicate that 50-90% of the incident kinetic energy can be lost on a single bounce. It was also thought that a concentration factor of 256 was too high and was leading to gas-phase scattering in the constricted region of the cone, thus reducing the effectiveness of the concentrator. The cones with the lower concentration factor near 12, proven to concentrate with the use of the pressure gauge, also showed a decrease in etching over the control. This decrease again could be accounted for by the low energy of the exiting O atoms and/or by gas-phase scattering in the concentrator resulting from the high peak flux of our pulsed O-atom source. In any case, the hope of using a cone-like structure to concentrate high-energy O atoms for accelerated testing or for novel film growth, whether in space or in a ground-based facility, has been significantly diminished.

The substantial amount of collaborative work done with Ionwerks has not yet led to any enabling technology. However, it is important that we have learned a counterintuitive lesson that the concentrators do not effectively concentrate. Without this knowledge provided by the PI's laboratory, Ionwerks would have proceeded blindly with a trial-and-error approach that would undoubtedly have consumed a great deal of time and money.

**Boeing.** Dr. Harold G. Pippin of Boeing had a similar idea as Dr. Shultz of Ionwerks to concentrate atomic oxygen. Dr. Pippin produced concentrators that were shaped like paraboloids rather than cones, and he had them flown on the MIR space station. His concentrators had concentration factors in the range of 8-16. Dr. Pippin has been concerned with the degradation of materials by atomic oxygen in low Earth orbit for about 15 years, and he saw a need for accelerated testing of candidate spacecraft materials in atomic oxygen environments. He had hoped that the concentrator would be efficacious; however, contamination around the MIR space station and changes in its altitude made the test inconclusive. Dr. Pippin was aware of the PI's research on atomic oxygen interactions with materials, and independently of Ionwerks, Dr. Pippin contacted the PI and arranged a ground-based test where Kapton was exposed through the Boeing concentrators. Exposures were performed with different atomic oxygen fluxes and with concentrators having different concentration factors. The exposed samples were delivered to Boeing, where the erosion yields were to be determined by profilometry. To date, Dr. Pippin has not reported the results to the PI, so it is not possible to compare the results on the Boeing concentrators to those of the Ionwerks concentrators. If the results are similar, then Boeing will undoubtedly rethink the idea of using a concentrator to conduct accelerated testing. Once again, the information provided by the PI may appear to be negative, but it was a relatively inexpensive test that could save Boeing time and money.

on a trial-and-error determination of the effectiveness of their concentrators. Regardless of the final outcome of this test, the work for Boeing has forged a relationship with Dr. Pippin that has already led him to include work for the PI in a large proposal for the development of new, atomic-oxygen-resistant, materials.

### **New discoveries, inventions, or patent disclosures**

Scientific discoveries have been summarized above and are described in the attached publications. No inventions or patent disclosures were made.

### **Honors/Awards**

Montana State University Alumni/Bozeman Chamber of Commerce Excellence Award for "inspirational influence on the achievements of Angela (Keefe) Frandsen."